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CERTAIN EFFECTS UNDER IRRIGATION OF
COPPER COMPOUNDS UPON CROPS*

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Part I.—EXPERIMENTAL WORK

INTRODUCTION

The region to which the studies described in this publication more particularly relate lies in southeastern Arizona in Greenlee and Graham counties and consists, first, of the Clifton-Morenci mining district and second, of the irrigated lands along the Gila River from twenty-five to sixty miles below. The Clifton-Morenci mining district is drained by Chase Creek into the San Francisco River, which in turn empties into the Gila. From the Gila, beginning at a point about twenty-five miles by channel below Clifton, irrigating waters are withdrawn for the use of the rich lands extending somewhat discontinuously from above San Jose to Fort Thomas, a distance of thirty miles. For about forty years, this up-stream mining district and the irrigated lands below have developed together from small beginnings into large industries.

Beginning with the initiation of smelting operations on the

San Francisco River in 1882, comparatively small amounts of mining detritus must have found their way into the irrigating water-supply. Following the discovery, in 1893, of immense deposits of low-grade sulphide ores in the district and the erection of concentrating plants to handle them, rapidly increasing quantities of fine slimes were discharged into the stream-flow, becoming noticeable in the irrigating waters of Graham County about the year 1900. Following the observation of their presence, various crop failures were attributed from time to time to the tailings, resulting finally in a request by the farmers of the district to the writer, for an examination of the facts relating to damage done by mining detritus to their irrigated crops.

SOLID WASTES

Following this request, the writer began a study of the problem in May, 1904, which resulted in the publication of Bulletin 53 of the Arizona Agricultural Experiment Station, September 20, 1906. This publication established the fact that irrigating sediments, in general, may be beneficial or harmful according to their composition and physical character and to the manner of their disposition in or upon the soil. If allowed to accumulate upon the surface of the soil in the form of more or less impervious silt-blankets, their influence, by limiting the supply of water and air to the soil, is notably harmful. In the case of the mining wastes from the Clifton-Morenci district, which are particularly plastic and "tight" in character, the damage done was found to be greater than that resulting from sediments arising from ordinary erosion. It was determined that the damage from these wastes, particularly to alfalfa and other crops which cannot receive constant and thorough cultivation, was of an increasingly serious character.

The farmers of Graham County, represented by one of their number, finally brought suit against the Arizona Copper Company, Limited, for discharging tailings into their irrigating water-supply. The case was decided in the District Court of Graham County in favor of the farmers, and an order was issued in November, 1907, effective May 1, 1908, restraining the mining companies from discharging "slimes, slickens or tailings" into

Chase Creek, the San Francisco River, or the Gila River. The case was appealed to the territorial Supreme Court where, however, the decision was confirmed in March, 1909. The case was again appealed by the Arizona Copper Company to the Supreme

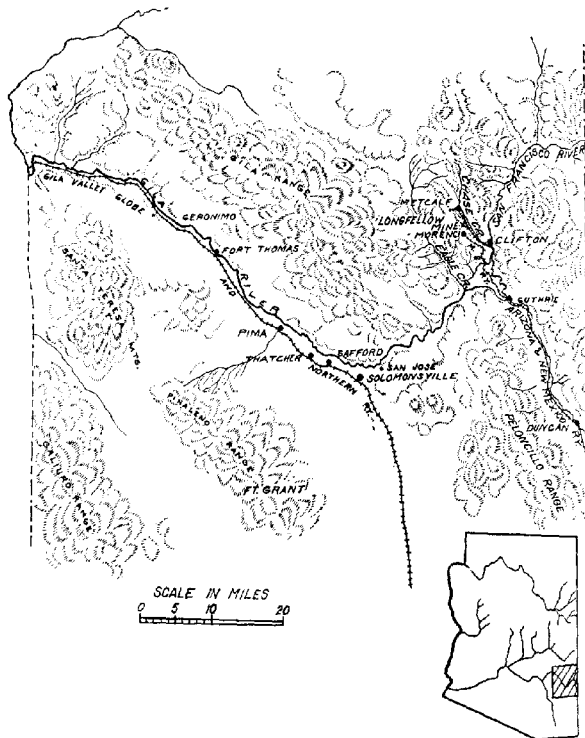


Fig. 1.—General map of the Clifton-Morenci and Gila River mining and irrigation district, Arizona

Court of the United States, where it was again and finally decided in favor of the farmers on June 16, 1913.

During and since the occurrences above mentioned, large quantities of solid wastes have been impounded by the copper companies in settling basins constructed for their storage in the

district. Recent investigations by the companies indicate a possibility that with copper at 15 cents a pound these stored tailings, which average about 0.85 per cent copper, may be profitably reworked.

In the long run, therefore, it may be found that an adjustment based upon a complete and impartial statement of facts relating to the tailings situation is beneficial both to the agricultural and to the mining interests concerned.

SOLUBLE COPPER COMPOUNDS

Following the disposition of mining detritus, there remained the problem of soluble copper compounds which, in small but continuously appreciable quantities, find their way with waste waters into the stream-flow of the region. These compounds originate in the ores of the district and are, as in the case of the carbonates, directly soluble to a slight extent in drainage waters, especially in the presence of carbon dioxide. In other cases, the original ores are changed through the action of air into soluble substances which then escape downstream. Sulphide ores are thus oxidized in the presence of air into soluble copper sulphate. Inasmuch as it is well known that minute amounts of copper in solution are extremely toxic to plant roots directly exposed to them, some apprehension naturally existed as to the effects of these small amounts of copper salts escaping into the water-supply of an irrigated district.

In some respects, conditions were especially favorable here to the successful prosecution of a study of the foregoing question. The irrigated lands are at a distance of twenty miles or more from the smelters, so that injurious gases could not complicate effects upon irrigated crops. There are, also, only traces of other toxic metals to be found within the district—more particularly, arsenic, antimony, and zinc. Injurious effects due to the possible toxic action of compounds originating in the mines are therefore limited to copper.

Scientific study relating to toxic effects of copper upon plants under varying conditions has thoroughly established not only the fact that copper compounds are extremely toxic to plants when they obtain entry to their tissues, but also that various

agencies standing between these poisonous salts and the living plant tend to prevent injury.¹ Soluble copper compounds, for instance, react with carbonate of lime, commonly abundant in soils of the arid region, to form the solid carbonates of copper. The partly decomposed silicates of these soils also precipitate soluble compounds of copper and mask their toxic character. Organic matter in the soil likewise holds large quantities of copper in comparatively harmless combinations. Through physical attraction or *adsorption*, soluble copper compounds enter into weak combination with fine soil particles and toxic effects are thereby greatly lessened. In the presence, also, of other soluble salts, such as the various forms of "alkali" commonly found in the soils of the region, the toxicity of copper compounds is enormously lessened.

The investigations recorded in this publication include: (1) Observations upon the distribution of copper in mining wastes, in irrigating waters, in soils and soil waters, in the plants, and in the animal life of the region. (2) The development of accurate methods for the determination of minute amounts of copper in all situations where they may occur. (3) Plant cultural work with waters and in soils in the presence of varying proportions of copper and under varying conditions. (4) A careful analytical study of the results of such cultures in order to determine the symptoms of poisoning and the distribution of copper throughout poisoned plants; and to identify, if possible, the particular parts of plants and tissues injured by copper. (5) A physiological study of plant reactions with copper. (6) Field studies for the purpose of relating the results of laboratory investigations to the question of economic injury done by copper salts to irrigated crops.

By reason of interruptions due to other duties, it has required a long time to mature this investigation to the point where it seems sufficiently complete for publication. This delay, however, has given perspective to the work and, especially, opportunity to verify earlier conclusions as applied to field conditions.

The writer is indebted for painstaking analytical work to Messrs. R. G. Mead, Edward E. Free, Dr. W. H. Ross and

¹ See Bibliography, pp. 487-488, references 1, 8, 14, 15, 16, 19, 34, 51.

C. N. Catlin, associated with the Arizona Agricultural Experiment Station from time to time; and to the helpful advice of Dr. Howard S. Reed, of the University of California Graduate School of Tropical Agriculture, in connection with the physiological part of the work herein described. The publication, also, has been criticized to its advantage by Dr. C. B. Lipman of the University of California.

DISTRIBUTION OF COPPER COMPOUNDS THROUGH- OUT THE CLIFTON-MORENCI AND GILA RIVER MINING AND IRRIGATION DISTRICTS

SOURCES OF COPPER

The original source of the copper found in this district, according to Lindgren,² is a Cretaceous or early Tertiary intrusion of acidic porphyries to which, in the Clifton-Morenci district, all ore deposits may be finally referred. The original porphyries contain as little as 0.02 per cent of copper ore in the form of chalcopyrite. Under the influence of superheated waters emanating from the porphyry, this chalcopyrite, together with other metallic compounds, was carried out from the molten intrusive mass into adjoining strata and there deposited, especially along fissures, in the form of concentrated masses or veins of chalcopyrite and other minerals. Through erosion these deposits were afterward subjected to atmospheric oxidation, followed by downward percolation and a period of secondary enrichment due to numerous reactions mainly between the oxidized compounds of copper and other minerals present.

In limestones and shales, these processes resulted in the formation of oxidized ores containing azurite, malachite, chrysocolla, and euprite. In porphyry, the main final result was chalcocite or copperglance, the principal constituent of the sulphide ores of the Clifton-Morenci district.

In general, therefore, the metasomatic changes associated, first, with superheated waters arising from the original intrusion of molten porphyry and, second, with meteoric waters percolating

² U. S. Geological Survey, Professional Paper No. 43, 1905.

downward with oxidizing effects through copper-bearing rocks, have brought copper from a concentration of possibly less than 0.02 per cent in the original porphyry through every degree of richness to the condition in some cases of pure copper.

PROCESSES BY WHICH COPPER IS ADDED TO THE WATER-SUPPLY

To a slight extent, drainage waters from the ore deposits and from the mines, containing considerable amounts of copper in solution, find their way downstream. But by far the larger part of the copper which gets into the irrigating supply is derived from the ores and tailings which, in the concentrators, on the dumps, and finally in the river itself, are subjected to the action of atmospheric oxygen, and water containing carbon dioxide and various salts in solution. The residual chalcocite in tailings from sulphide ores thus reacts with oxygen from the air and yields copper sulphate in solution. This, in turn, reacts with the excess of bicarbonate of lime ordinarily contained in the waters of the San Francisco and Gila rivers. The resulting basic carbonate of copper is notably soluble in water containing carbon dioxide and certain of the various salts commonly found in river waters. The residues of carbonates of copper in oxidized ores are directly dissolved in waters containing carbon dioxide and certain soluble salts.

Along with minute quantities of copper thus dissolved and carried forward, pass the solid residues discharged from the concentrators—solid wastes which find their way, unchanged, downstream and finally upon the soils of irrigated fields. At this point begins another and very important series of reactions between dissolved copper compounds and the soil, tending in general to withdraw copper from its solutions and precipitate it in the form of less harmful solid compounds. These are briefly referred to above and will be discussed more in detail further on in this paper. Opposing these precipitations of copper are those solvents which tend to maintain this metal in soluble form in small quantities in the soil. Chief of these is carbon dioxide, which is always present in agricultural soils in significant quantities. Of interest in this connection is the fol-

TABLE I
SOLUBILITIES OF COPPER COMPOUNDS

Compound	Solvent	Cu dissolved, parts per million	Reference
Malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Water containing 0.12% carbon dioxide	29.0-31.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1367
Precipitated basic copper carbonate	Pure water	1.5	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1370
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide	34.8	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1370
Precipitated basic copper carbonate	Water containing 0.13% carbon dioxide and 0.01% sodium chloride	36.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1371
Precipitated basic copper carbonate	Water containing 0.13% carbon dioxide and 1.0% sodium chloride	58.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1371
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide and 0.01% sodium sulphate	37.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1372
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide and 1.0% sodium sulphate	58.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1372
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide and 0.01% sod. carbonate	10.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1372
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide and 1.0% sod. carbonate	0.7	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1372
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide and 0.2% calcium sulphate	36.0	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1372
Precipitated basic copper carbonate	Water containing 0.12% carbon dioxide and 0.11% calc. carbonate	1.4	E. E. Free, Journ. Am. Chem. Soc., XXX, 9, p. 1372
Copper sulphide; CuS	Oxygen-free water	0.09	W. H. Ross, MSS
Chalcopyrite CuFeS ₂	Pure water	measurable amounts	U. S. Geol. Survey Monograph XLVII, p. 1107
Chalcopyrite CuFeS ₂	Sodic sulphide	Amt. not stated	U. S. Geol. Survey Monograph XLVII, p. 1106
Malachite	"Insoluble in water, slightly soluble in water charged with carbon dioxide."		Moissan 5, p. 167
Chrysocolla $\text{CuSiO}_3 \cdot n \text{H}_2\text{O}$	"Somewhat soluble in water with carbon dioxide"		Lindgren, U. S. G. S. Prof. paper 43, p. 188
Cupric sulphide CuS	Water	1 to 950,000	Comey, Dict. Solu- bilities, p. 139
Cuprite Cu ₂ O	"Insoluble in water"		Comey, Dict. Solu- bilities, p. 137
Cuprie oxide CuO	"Insoluble in water"		Comey, Dict. Solu- bilities, p. 137

lowing table of solubilities of various compounds of copper in different solvents, made up from different sources of information. The exact determinations of solubility by E. E. Free and W. H. Ross were made to obtain data needed in this investigation.

This table indicates that the carbonates and the silicate (chrysocolla) of copper, which are the compounds in which the metal must largely occur in the soil, are notably soluble in aqueous solutions of carbon dioxide.³ Large amounts of sodium chloride and sodium sulphate increase the solubility of precipitated basic copper carbonate. In pure water, copper compounds, so far as observed, are but slightly soluble. Fluctuations in the content of carbon dioxide and of soluble salts in soil waters, and variations in the character of the soluble salts, are shown to affect the copper content of such waters.

In brief, the final effect upon plant roots of copper in the soil is the complex resultant of many opposing influences tending, on the one hand, to remove copper from solution, and, on the other, to maintain it in toxic soluble form. *Observations on the soil* usually fail to give satisfactory evidence as to the toxic or non-toxic effects to be expected from small percentages of copper that may be present. *Direct chemical and physiological studies of plants* afford much more satisfactory information. This mode of attack has been employed considerably in this investigation.

In view of the general tendency in nature to hinder the movements of copper in soils and to convert it into its insoluble forms, and independently of any tendency of the plant itself to assimilate or to reject copper, we should expect to find relatively small amounts of this element in plant tissues.

The following analytical determinations of copper in ores and tailings were made in samples carefully collected by the writer throughout the district studied. In all cases, the copper was determined electrolytically, manipulations of great delicacy having been developed for the determination of the minute amounts of copper often encountered. A full statement of the methods of preparing samples for analysis, and of determining

³ Sullivan has shown that powdered silicates react with copper sulphate to withdraw copper from solution; and that this copper will then be redissolved by a solution of potassium sulphate. U. S. Geol. Survey, Bull. 312, 1907.

copper in ores, tailings, waters, soils, and organic materials, is to be found under "Methods of Analysis" in the appendix to this paper. For convenience in comparing widely variable amounts in the samples examined, the copper content is given in parts per million of substance. Parts per million may be reduced to percentages by moving the decimal point four places to the left. For instance, 11,600 parts per million is equal to 1.16 per cent.

TABLE II
COPPER IN ORES AND TAILINGS FROM THE CLIFTON-MORENCI MINING DISTRICT

Sample No. and date	Description of sample	Condition and weight taken, grams	Cu found, grams	Cu parts per million
3491	One day's run of sulphide ore from	1		
May 23, '04	from A. C. Co.'s mill in Clifton	air-dry	.03195	31,950
3303	Sulphide tailings, point of discharge	1		
May 23, '04	from A. C. Co.'s mill, Clifton	water-free	.00935	9,350
3438	Sulphide tailings, point of discharge	1		
June 28, '05	from A. C. Co.'s mill, Clifton	water-free	.0116	11,600
3499	Sulphide tailings at Clifton coming	1		
June 28, '05	from Longfellow mill	water-free	.00725	7,250
D. C. Co.'s Records	Fine sulphide tailings at Morenci			10,000
May 20, '04				
3492	One day's run of oxidized ore from	1		
May 23, '04	A. C. Co.'s mill at Clifton	air-dry	.0553	55,300
3304	Oxidized tailings, point of discharge	1		
May 23, '04	from A. C. Co.'s mill, Clifton	water-free	.0225	25,500
3439	Oxidized tailings, point of discharge	1		
June 28, '05	from A. C. Co.'s mill, Clifton	water-free	.0268	26,800
3500	Oxidized tailings, point of discharge	1		
June 27, '05	from Shannon C. Co.'s mill, Clifton	water-free	.0114	11,400
3309	Milky sediments, pure tailings from	2		
May 26, '04	Montezuma Canal, Solomonville	water-free	.01725	8,625
3486	River sediments with tailings from	2		
June 11, '05	Montezuma Canal, Solomonville	water-free	.0067	3,350
3737	High river sediments with muddy			
Feb. 22, '07	tailings from Montezuma Canal, Solomonville	15.8 water-free	trace	trace
6342	Floodwater sediments from Monte-			
Mar. 4, '16	zuma Canal, Solomonville; tail- ings from Mogollon	.5899	.000085	53

A point of interest to both mine owners and farmers in table II is the large proportion of copper that was discarded with tailings at the time the samples were taken. This loss, so far as these figures show, may amount to almost one-third of the copper

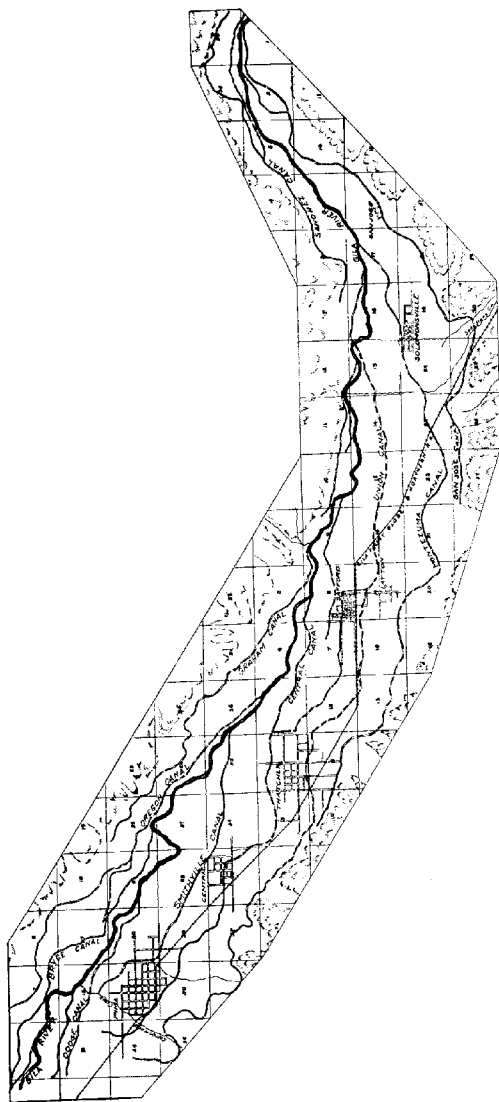


Fig. 2.—Detail map of the Gila River irrigation district, in Graham County, Arizona.